



# Carbonic springs as distal manifestations of geothermal systems, highlighting the importance of fault pathways and hydrochemical mixing: Example from the Jemez Mountains, New Mexico

Chris McGibbon\*, Laura J. Crossey, Karl E. Karlstrom, Tanner Grulke

Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA

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## ABSTRACT

We examine a series of carbonic warm and hot springs in northern New Mexico, USA: 1) Tierra Amarilla springs 2) Penasco Springs and 3) Soda Dam, Jemez and Indian hot springs. Spring geochemistry is compared to waters from the Valles Caldera geothermal system and to groundwater in nearby sedimentary aquifers. Multiple hydrochemical tracers are applied to quantitatively evaluate flow paths and mixing at varying distances from the caldera. We test three hypotheses for source and transport of waters to Tierra Amarilla and Penasco Springs: San Juan basin origin, meteoric flow from the Nacimiento Mountains, and/or influence from the Valles Caldera geothermal system. Geochemically, carbonic spring groups are distinct from meteoric and sedimentary aquifer waters. Based on isotopes of He and Sr, and concentrations of Cl, SO<sub>4</sub>, Li and B, we interpret these carbonic springs to be distal manifestations of fluid circulation along faults with a mixture of Valles Caldera geothermal waters, local meteoric and Paleozoic aquifer waters, with the potential for small contributions from the San Juan Basin aquifers. Semi-confined fault conduits, the Jemez fault and Nacimiento fault systems, provide connectivity and help explain geochemical similarities and mixing trends within carbonic spring systems, and between these systems and the distal Valles Caldera. In addition, Penasco Springs are interpreted to reflect a component of outflow from the geothermal system that crosses the Nacimiento Mountain basement block along NE-trending faults. Input of deeply sourced waters can degrade water quality by contributing significant salinity and trace metals to groundwater at distances of > 50 km from geothermal systems, with faults acting as conduits for subsurface fluid flow.

## 1. Introduction

In the face of climate change, water managers in the American Southwest face increasing pressure to accurately forecast water supply (Gutzler, 2007) and water quality (Crossey et al., 2012). Understanding the source, movement, and controls on water quality is multifaceted. Additionally, hydrologic flow models show the complexities that faulting brings to fluid migration pathways (Banerjee et al., 2011). Integrated studies using a multi-parameter approach are required to identify fault pathways and their influence on springs, surface water and groundwater (Caine et al., 1996; Herczeg and Edmunds, 2000). Numerous studies combining natural tracers have shown evidence of groundwater upwelling and associated fault fluid circulation and migration (Chiodini et al., 1999; Crossey et al., 2009; Gardner et al., 2011; Phillips et al., 2003; Williams et al., 2013). In particular, the presence of mantle volatiles in carbonic springs (Newell et al., 2005; Crossey et al.,

2009, 2011, 2016) provides direct evidence of a deep connection. Deeply sourced, or endogenic, fluids obtained from below regional freshwater aquifers contribute elevated salinity, trace metals, CO<sub>2</sub>, <sup>87</sup>Sr/<sup>86</sup>Sr and mantle-derived He (Newell et al., 2005; Williams et al., 2013), and can effect both local and distal groundwater as determined by fault connectivity, the nature of the flow paths, mixing, and spring discharge.

Regional studies show the importance of deep groundwater inputs on surface water quality. Across the western U.S., groundwater that carries mantle volatiles (as evidenced by helium isotope values) are highly saline and poor quality with elevated trace metals, such as arsenic (Newell et al., 2005). Numerous workers (Phillips et al., 2003; Hogan et al., 2007; Kirk et al., 2009; Williams et al., 2013) established that salinity contributions from upwelling groundwater degrade water quality in the Rio Grande; while Crossey et al. (2009) and Karlstrom et al. (2013) used helium isotope ratios and CO<sub>2</sub> to identify endogenic

\* Corresponding author.

E-mail address: [mcgibbon@unm.edu](mailto:mcgibbon@unm.edu) (C. McGibbon).

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inputs to geothermal springs in Arizona and Colorado. Mantle tomography of the U.S. (Schmandt and Humphreys, 2010) shows low relative P wave velocities in northern New Mexico and below the Valles Caldera. Low velocity zones are thought to contain small but significant fractions of partial melt and volatiles (Schmandt and Humphreys, 2010), and have been associated with neotectonic mantle degassing in southern Colorado (Karlstrom et al., 2013) and across the western U.S. (Crossey et al., 2016) based on correlation of high  $^3\text{He}/^4\text{He}$  ratios with low P-wave velocities.  $\text{CO}_2$  springs and travertine deposits represent near-surface manifestations of volatile transfer from the mantle to the near-surface hydrologic system in regions associated with domains of low mantle velocity (Karlstrom et al., 2013). Chiodini et al. (1999), Crossey et al. (2009) and Karlstrom et al. (2013) have all used carbon isotope values to identify the sources of carbon and provide evidence for the relative proportions of different carbon sources in carbonic springs.

This study focuses on carbonic warm and hot springs (20–60 °C) in northern New Mexico that are situated at the nexus of three physiographic provinces: the Rio Grande rift, southern Rocky Mountains, and Colorado Plateau. The study area provides a unique field laboratory where the interaction of multiple hydrologic flow paths can be studied. Three groups of artesian,  $\text{CO}_2$ -rich travertine-depositing springs are examined (Figs. 1 and S1): 1) Tierra Amarilla (TA) anticline spring group near San Ysidro, 2) Penasco Springs group (PS) on the west side of the Nacimiento uplift, and 3) Soda Dam springs (SDS), Jemez Springs (JS), and Indian hot springs (IS) within the Jemez Mountains. The Tierra Amarilla group, farthest from the Valles Caldera, consists of warm springs aligned N–S in the core of the Tierra Amarilla anticline (Hart, 2001; Cron, 2011). The Penasco Springs, west of the Nacimiento Mountains, also warm carbonic springs, are along strike and farther north, but also aligned on the N–S trending Nacimiento fault. The third group of springs discharge in multiple locations along the Jemez River in the San Diego Canyon, are aligned along the NE-striking Jemez fault zone (Kelley et al., 2007), and are considered part of the outflow of the Jemez hydrothermal system (Goff et al., 1981; Trainer, 1974).

Previous workers have concluded that groundwater discharging along the Nacimiento fault (TA and PS spring groups) is sourced from the San Juan Basin (Fig. 1; White, 1985; Goff et al., 1986; Dam, 1995). This hypothesis was inferred from groundwater flow directions based on potentiometric contour lines (Fig. 1) of aquifers in the Cretaceous and Jurassic rocks of the south eastern San Juan Basin that indicate a general southeasterly flow direction (Frenzel and Lyford, 1982; White, 1985). A second hypothesis (Hart, 2001) is that springs along the Nacimiento fault are derived from flow down the southern Nacimiento mountains along the dip-slope of the Agua Zarca sandstone aquifer (Fig. 1). In this hypothesis, the water for carbonic springs is of dominantly meteoric origin and the carbonic character is gained through water-rock interaction along the flow path. A third hypothesis (Renick, 1931) is that Nacimiento fault springs are sourced, at least in part, from the Valles Caldera hydrothermal system (Figs. 1 and S2). In this hypothesis, the source of the  $\text{CO}_2$  and the elevated temperature is the magmatically driven Valles Caldera hydrothermal system and its outflow plume that flows southwest from the caldera, down the San Diego Canyon.

The goal of this paper is to assess similarities and differences between spring groups to evaluate source regions, flow paths, hydrologic mixing and importance of faults, and thereby test the three hypotheses. The broader study area has seen extensive study, in particular the proximal Valles Caldera as a potential geothermal resource, however less attention has been paid to carbonic springs that are distal to the caldera. We use a suite of natural tracers to evaluate temporal and spatial variations in chemical, gas and isotopic composition to examine the importance of fault conduits for fluid transport and for mixing of deeply sourced fluids in groundwater systems. This work has implications for water quality, land use, and geothermal potential of this and other regions.

## 2. Study area

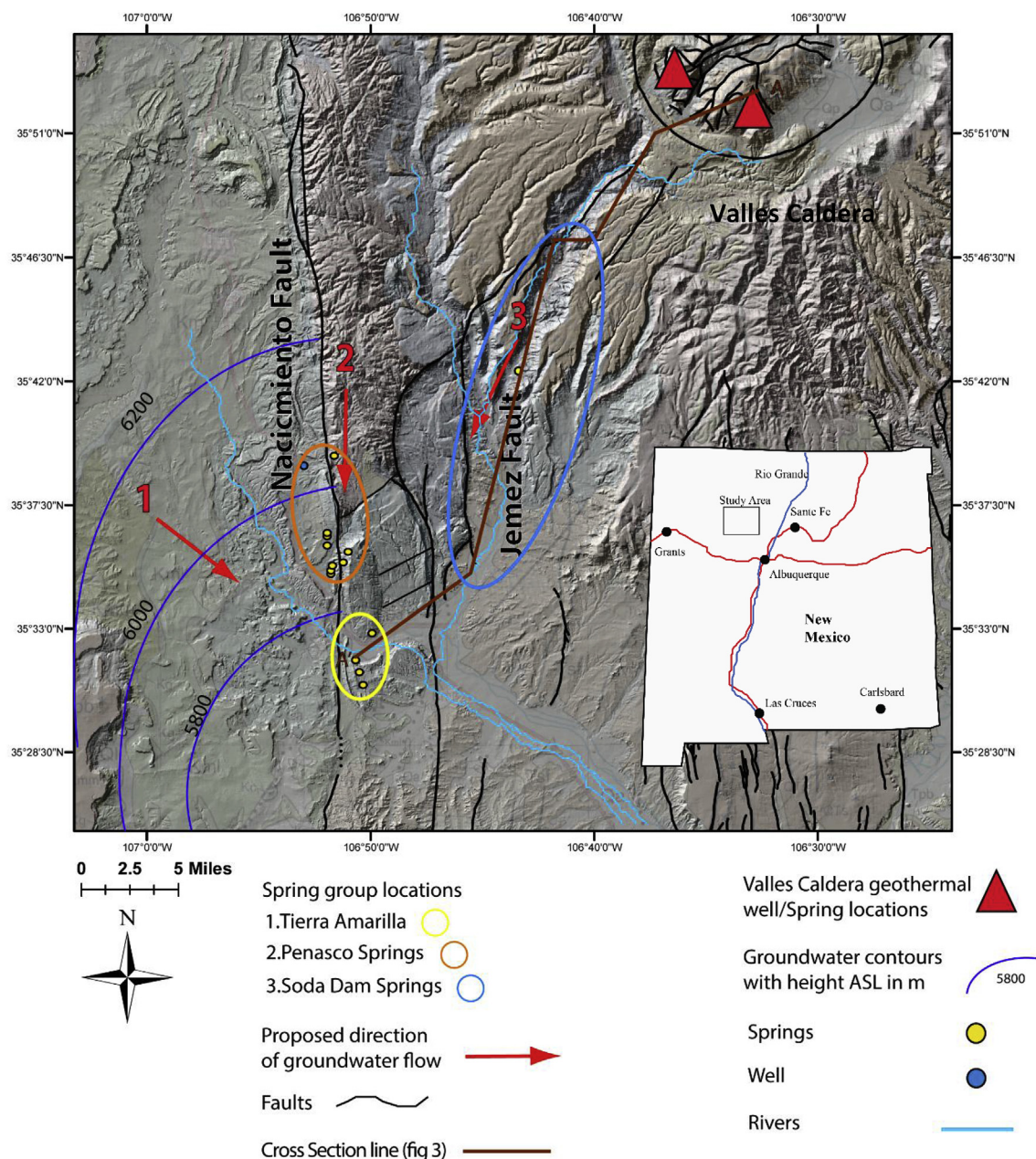
### 2.1. Regional geology and hydrostratigraphy

The geologic map and regional stratigraphy are shown in Figs. S3 and S4, with major hydrostratigraphic units highlighted. The Laramide-age Tierra Amarilla anticline is an approximately 1.6-km-long north-trending fault-cored anticline. To the north, the Nacimiento uplift, is a north-south trending 80-km-long, 10–20-km-wide east-tilted uplifted basement-cored block bounded on the western side by the Nacimiento fault system (Woodward, 1987). The southern end of this uplift terminates in a large south-plunging fold beneath unconformable Tertiary rocks (Slack, 1973). To the west, the San Juan Basin forms the south-eastern margin of the Colorado Plateau; its eastern boundary is marked by the Nacimiento uplift. To the southeast, the Rio Grande rift comprises a series of north-trending grabens and half grabens, which extend from Colorado to the boarder of Mexico (Kelley, 1952; Chapin and Cather, 1994). The Jemez Volcanic field and Valles Caldera are located along the western rift fault. On a large scale, Valles Caldera was built on the western edge of the Rio Grande rift at its intersection with Jemez lineament (Heiken et al., 1990). The Jemez Volcanic field consists of basaltic to rhyolitic rocks erupted from > 13 to 0.13 Ma (Zimmerer et al., 2016 and references therein).

The hydrostratigraphic units include the Madera Group limestone, a fractured carbonate aquifer where groundwater flow is concentrated along discrete fractures, fracture systems, or bedding planes. Above this the Abo and Yeso formations act as a confining layer (Crouch, 1994) between the Madera and the San Andres-Glorietta aquifers. This aquifer may also be important east of Nacimiento fault and at depth in the San Juan Basin. The Chinle shale is the confining unit below the Nacimiento fault springs and the Agua Zarca is an important aquifer in the southern Nacimiento Mountains as it forms a southern dip-slope to the anticlinal uplift. The Jurassic Entrada Sandstone forms an isolated aquifer in the San Juan Basin that is stratigraphically separated by aquitards of mudstone, shale, and siltstone, and by lateral discontinuities produced by north-south faults. Many of the aquifers exhibit elevated temperature, up to 25 °C.

### 2.2. Geothermal setting

The Valles Caldera contains a magmatic hydrothermal system with well-characterized geothermal fluids. Numerous workers have investigated the hydrothermal aspects of the Valles Caldera (Lambert and Epstein, 1980; Goff et al., 1981, 1986, 1988, 2002; Hulen and Nielson, 1986; Heiken et al., 1990; Shevenell, 1987; Vautaz and Goff, 1986), but less attention has been given to the distal effects of the hydrothermal system, particularly connected to fault-related fluid circulation and mixing (Cron, 2011). Briefly, a hydrothermal outflow plume from the Valles Caldera has been suggested (Dondanville, 1971; Trainer, 1974) with geochemical evidence from springs in this location, including Soda Dam and Jemez Springs, providing support for this idea (Goff et al., 1981). The depth of hydrothermal circulation in the outflow is believed to be in excess of 2000m, with temperatures reaching 330 °C and a plume extending down San Diego Canyon at least as far as Jemez Springs and potentially further (Goff et al., 1988; Trainer et al., 2000). In this model, (Fig. S2), meteoric water recharges the geothermal system, then rises by convection to depths of 600 m or less. Fluid flows out of the caldera, towards the west and southwest, under the Jemez Plateau and along the Jemez fault zone, where it mixes or discharges as hot springs in the San Diego Canyon (Dondanville, 1979; Goff et al., 1985, 1988; Ingebritsen et al., 2006; Trainer et al., 2000). Two distinct zones are identified within the Valles Caldera, the Sulfur Springs area and Redondo Creek Baca wells; The latter of which is considered to consist of two subsets of hydrothermal fluids based on temperature and geochemistry. Wells drilled in the Valles Caldera show the plume to occur in the Madera Group limestone, whereas outside of the Caldera,



**Fig. 1.** DEM (Earth Data Analysis Center) of study area with alternative models for groundwater flow directions to be tested: 1) San Juan basin flow path showing water table contours (Frenzel and Lyford, 1982); 2) meteoric water from Nacimiento Mountains; 3) hydrothermal plume from Valles Caldera. Main spring groups are shown by ovals. NE-SE line shows location of the cross section of Figure S2. Inset map shows study location in state.

the plume surfaces near the Jemez River in springs located in eroded folds and fault blocks (Trainer et al., 2000). Small, local, low-to-moderate temperature geothermal reservoirs of low volume are also found along the Jemez fault zone (Goff et al., 1981).

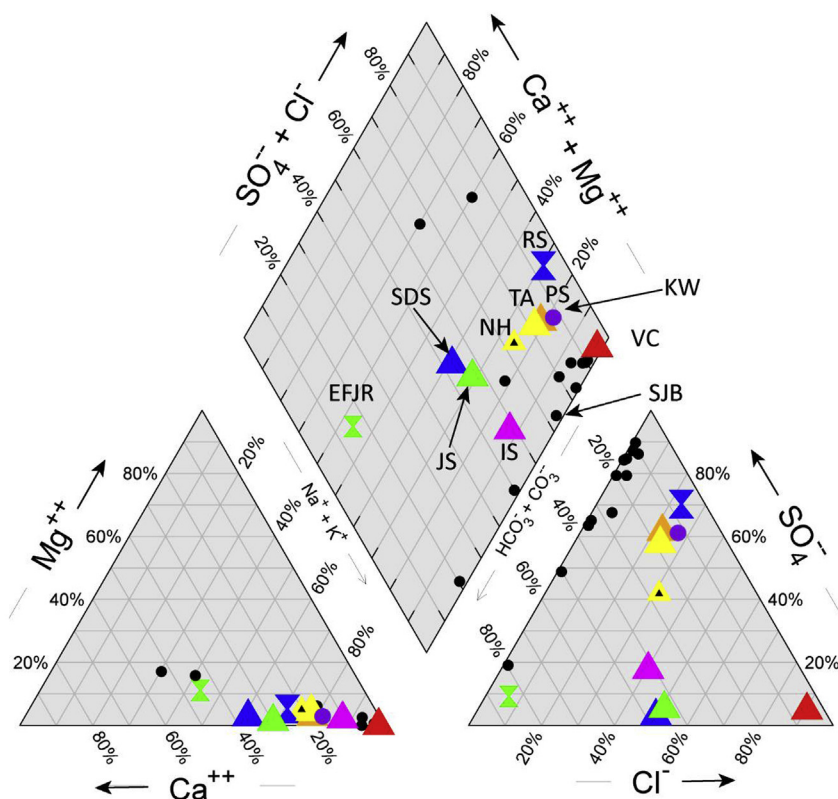
The extent of influence of geothermal waters in the carbonic springs within San Diego Canyon has been debated (Goff et al., 1988). An interesting conundrum about the Soda Dam springs group of hot springs and wells is that, if they are manifestations of the Valles Caldera geothermal outflow plume, there are not simple NE to SW trends in temperature and fluid chemistry along San Diego Canyon, as Jemez Springs is further down the canyon, but warmer and less saline than Soda Dam, such that mixing of multiple fluids is required. The distal extent of this geothermal outflow plume has been debated, with some workers suggesting the Tierra Amarilla and Penasco Spring groups are unrelated to geothermal outflow (Goff et al., 1981). This is partially semantic in terms of defining mixing proportions at the distal end of a geothermal

outflow plume, but evaluation of such mixing is also of practical importance in terms of geothermal exploration (for example the recent \$5M DOE drill hole on Jemez Pueblo; Kaufman (2011)) and in terms of potential degradations to surface and groundwater quality (Crossey et al., 2012). Goff et al. (1981) concluded that, based on ion ratios and Cl variation diagrams that San Ysidro mineral waters (Tierra Amarilla Springs) are not derivatives of the Valles Caldera, but originate from a separate low temperature system, discharging along the Nacimiento fault, whereas this paper explores the possibility a direct connection to the geothermal system.

### 2.3. Springs

The spring groups examined are near the northwestern portion of the Albuquerque Basin whose boundary with the Nacimiento uplift is a series of north-to northeast-trending faults (Woodward, 1987). Details





**Fig. 2.** Piper diagram showing water samples in context of the broader study area. TA – Tierra Amarilla (large yellow triangle), NH – North Highway (smaller yellow triangle with black center), PS – Penasco Springs (orange triangle), KW – Kasemen Well (purple circle), SDS – Soda Dam spring (blue triangle), JS – Jemez Springs (green triangle), IS – Indian hot springs (pink triangle), VC – Valles Caldera (red triangle), RS – Rio Salado (blue X), EFJR – East Fork Jemez River (green X), SJB – San Juan Basin (black dots). Mean sample data are used for TA, PS, SDS, JS, IS and VC. TA and PS springs samples cluster together alongside samples from SDS and JS. San Juan Basin waters plot in variable locations suggesting variable aquifer sources. Kasemen Well (KW) shows similar chemistry to TA/PS (individual spring Piper diagrams are in fig DR-2). (For interpretation of the references to colour in this Fig. legend, the reader is referred to the Web version of this article.)

of the spring groups studied are depicted in Fig. 1 (greater detail in Fig. S1). Two of the spring groups occur along the Nacimiento fault zone both north and south of the Rio Salado: the northern Penasco Spring group and the southern Tierra Amarilla springs group. Within the Tierra Amarilla springs group, three springs are collinear and located along the fault that cores the Tierra Amarilla anticline, and one is off axis of the fault. The latter, North Highway spring, is also noted as being chemically distinct from the rest and with greater variation in chemistry (see below). This spring lies at the foot of the dip-slope of Agua Zarca on the south-plunging fold of the southern Nacimiento uplift. Where the springs discharge, they form pools within travertine mounds and cisterns whose depth range from ~0.2 m to up to ~8 m. The sizes of the spring orifices vary along their long axis from ~0.1 m to up to ~10 m. Travertine occurs at all locations, and many inactive springs are represented by dry travertine mounds and vent orifices. Degassing of CO<sub>2</sub> is witnessed as bubbling at most springs. U-series age geochronology at the Tierra Amarilla anticline shows that the springs have been active intermittently from before 270 ka, at highest elevations, to modern actively forming mounds (Cron, 2011). Little vegetation grows around the springs, and the pool surfaces are often found at depth below ground level, in collapsed travertine mounds, in some cases, up to 30 m deep, indicating that the water elevations were higher in the past (Cron, 2011). All springs are at ~100 m higher elevation than the proximal Rio Salado, indicating artisan characteristics. This elevation and the co-alignment along the fault indicate a confined or semi-confined aquifer sealed by the Triassic Chinle Formation and with fluid movement along the fault.

### 3. Methods

#### 3.1. Water and gas sampling

We sampled a subset of the springs on multiple occasions over a one year period from November 2013 to October 2014. These raw data are synthesized with historical hydrochemical data (Supplementary

material tables). Water sampling was carried out following procedures set out in USGS National Field Manual for the Collection of Water-Quality Data (2006). Water samples for cations and <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratios were collected in 60 mL High Density Polyethylene bottles (HDPE). Samples were filtered (0.45 μm) and acidified using concentrated HNO<sub>3</sub>. Samples for anion, alkalinity and δ<sup>18</sup>O and δD isotope analysis were collected without headspace in 120 mL HDPE bottles. Direct gas sampling for concentration and isotope ratio (exsolved gases) for δ<sup>13</sup>C–CO<sub>2</sub> and He was carried out by submerging a plastic funnel over bubbling springs with gases then drawn into refrigeration-grade copper tubes that were flushed in-line before sealing with stainless steel clamps (Giggenbach and Goguel, 1988; Hilton et al., 2002).

#### 3.2. Analytical methods

Water temperature, pH and specific conductance were measured using an Oakton waterproof pH/CON 300 multi-meter. Major ion chemistry was analyzed using inductively coupled plasma optical emission spectroscopy (cations) and ion chromatography (anions) using standard methods, comparable to US EPA 200.7 and EPA 300.0 respectively. Carbonate alkalinity was measured by titration using standard methods (American Public Health Association, 1995). These analyses were carried out at the Analytical Geochemistry Laboratory at the University of New Mexico (UNM). Stable isotope analysis of D and <sup>18</sup>O were carried out using cavity ring-down spectroscopy (Picarro L1102-I) with methods comparable to Wassenaar et al. (2012) at the Center for Stable Isotopes, UNM. <sup>87</sup>Sr/<sup>86</sup>Sr ratios were determined on a Neptune MC-ICP-MS using methods comparable to Pin and Bassin (1992) at the Radiogenic Isotope Geochemistry Laboratory at UNM. Total CO<sub>2</sub> and He concentration and the isotopic ratio <sup>3</sup>He/<sup>4</sup>He and <sup>13</sup>C/<sup>12</sup>C–CO<sub>2</sub> were analyzed at the Fluids and Volatiles Laboratory at Scripps Institution of Oceanography using a noble gas isotope ratio mass spectrometer and electrostatic analyzer. <sup>3</sup>He/<sup>4</sup>He ratios (R) are normalized to the atmospheric value (R<sub>A</sub>), and corrected for air-derived He (to R<sub>c</sub>/R<sub>A</sub>) using the correction factor X = [(He/Ne)<sub>sample</sub>/(He/Ne)<sub>air</sub>] × (β<sub>Ne</sub>/

**Table 1**

Mean and standard deviation for spring parameters (units in table) and major ion chemistry (ppm).

Spring Name		Temp °C	pH	SpCond $\mu\text{S}/\text{cm}$	Ca	Mg	Na	K	HCO <sub>3</sub> <sup>3</sup>	Cl	SO <sub>4</sub>
Tierra Amarilla	Mean	21.4	6.0	12741	383	90	3010	111	2083	2395	2940
	Std. Dev.	2.7	0.1	2949	92	49	822	42	365	515	1198
Penasco Springs	Mean	24.9	6.3	13434	335	56	2705	84	1477	2288	2963
	Std. Dev.	4.1	0.2	1252	96	14	892	27	402	682	966
Valles Caldera	Mean	203.4	7.3	19707	21	0	1893	334	174	3169	43
	Std. Dev.	99.9	1.0	34363	27	1	353	127	86	561	12
Soda Dam Springs	Mean	43.4	6.4	6574	321	25	926	166	1390	1460	42
	Std. Dev.	6.4	0.3	572	44	8	97	23	225	118	9
Jemez Springs	Mean	65.9	6.6	3857	134	6	557	63	685	812	71
	Std. Dev.	10.6	0.3	763	20	2	135	13	93	210	135
Indian Springs	Mean	31.3	6.8	5086	75	15	1204	58	1285	1239	273
	Std. Dev.	13.0	0.4	3716	13	8	811	36	531	772	166
San Juan Basin	Mean	25.5	8.5	nr	54	15	251	2	296	59	437
	Std. Dev.	7.7	0.4	nr	53	15	251	1	65	98	375

$\beta_{\text{He}}]$ , where  $\beta$  = Bunsen solubility coefficient (see Hilton (1996) for details of the correction protocol). Geochemical modeling for saturation indices was carried out using Phreeqc (Parkhurst, 1995).

## 4. Results

### 4.1. Water chemistry

Sample locations, field parameters and water chemistry are listed in Tables S1 and S2 and shown in Fig. 2 (and Fig. S1) and mean values are in Table 1. At Tierra Amarilla springs, pH ranges from 5.38 to 6.94, temperature from 16.7 to 27.7 °C and conductivity from 7400 to 20,000  $\mu\text{S}$ . It should be noted that whilst the range of temperatures and conductivities between springs is quite large, variation within each spring is relatively small. Temperature variations track seasonal change to varying degrees, and at Twin Mound East are less than 1 °C over the course of the year, while conductivity variations within each spring are on the order of ~3,000–4,000  $\mu\text{S}$ . Penasco Springs are similar to Tierra Amarilla springs; pH 6.02–6.63; temperature 19.1–34 °C and conductivity 5,800–7,420  $\mu\text{S}$ . The carbonic springs are consistent through time in temperature, pH, and conductivity such that variations between springs and spring groups are interpreted to reflect different flow paths and mixing histories. Tierra Amarilla and Penasco Spring have overlapping major ion chemistry and are Na + K–SO<sub>4</sub>+Cl dominated (Fig. 2). At Tierra Amarilla, North Highway shows a different chemistry, having 15% less SO<sub>4</sub> relative to the rest of the springs. Soda Dam and Jemez Springs have higher Ca and HCO<sub>3</sub> in comparison to Tierra Amarilla and Penasco Springs, but are Na + K–SO<sub>4</sub>+Cl dominated. Indian hot spring samples have relatively higher Na + K with SO<sub>4</sub> values that fall in between Tierra Amarilla/Penasco Springs and Soda Dam/Jemez Springs. Valles Caldera waters are Na + K–Cl dominated, typical of geothermal brines. San Juan Basin waters are dominantly Na + K–SO<sub>4</sub>, but have a range of different chemistry, depending on the aquifer. The spring groups form distinct clusters (Figs S5 a–e and S6 a–g), different from surface and sedimentary aquifer waters, which indicate significant groundwater geochemical variability.

### 4.2. Conservative tracers

Conservative tracers used to characterize geothermal systems include Li, B and Br (Table S4, mean values in Table 2), and cross plots of these elements (vs Cl) are shown in Fig. 3 a–c (and Fig. S7 a–c). Previous studies (Goff et al. p241, 1981; Trainer et al., p88, 2000) used these conservative tracers (lower Li and Li/Na ratio) and Cl concentrations (Tierra Amarilla/Penasco Springs, 1,500–3,800 mg/L, compared to Soda Dam springs/Jemez Springs, 200–1,800 mg/L) to suggest Tierra Amarilla/Penasco Springs are not sourced from the Valles Caldera. Our new data show a more overlapping range and although these plots

**Table 2**

Mean and standard deviation for trace element chemistry. No data for San Juan Basin springs (ppm).

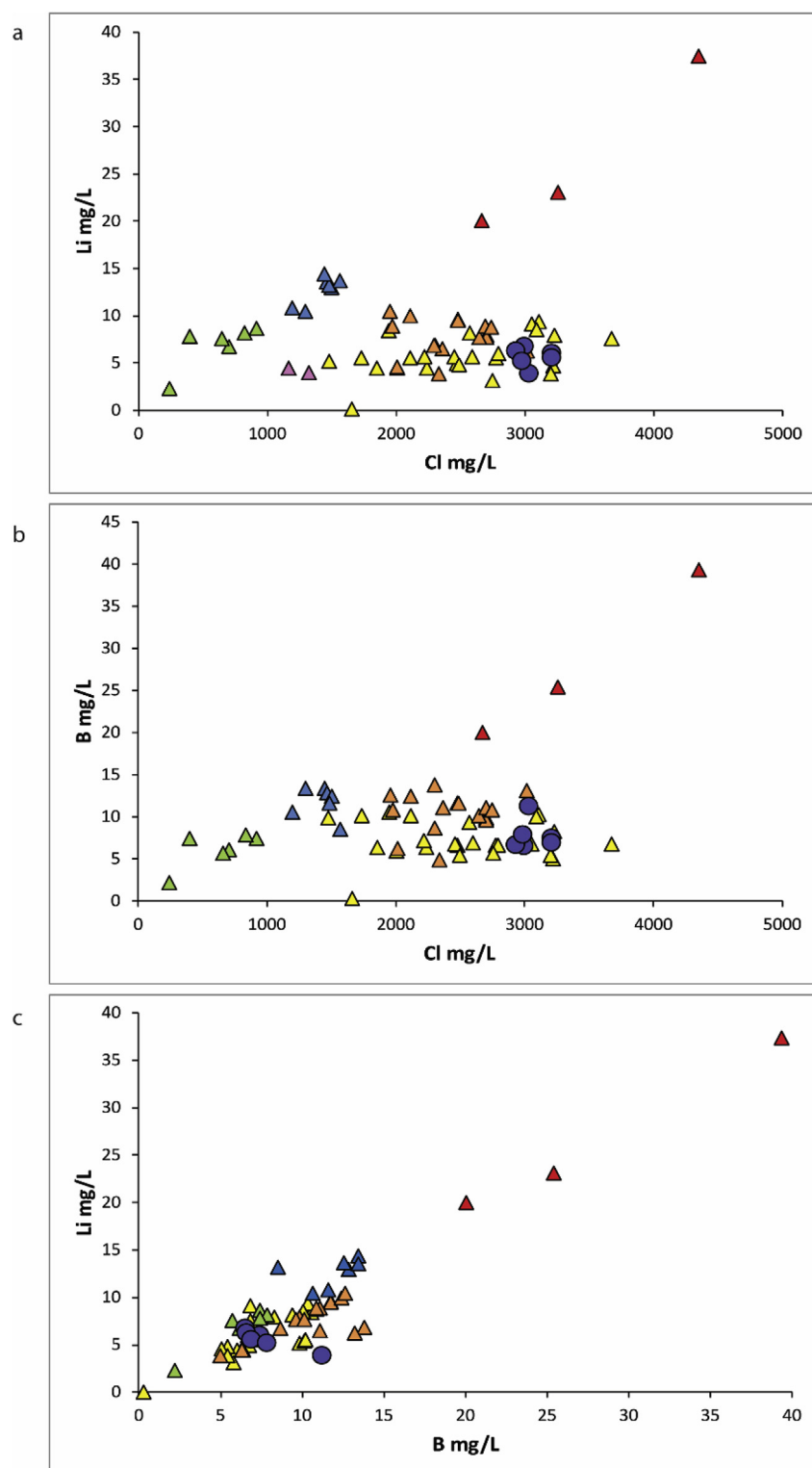
Spring Name		Li	B	Br	Si	Sr
Tierra Amarilla	Mean	5.7	7.5	4.5	6.4	6.7
	Std. Dev.	2.3	2.7	2.3	2.3	4.6
Penasco Springs	Mean	8.2	10.5	4.2	11.4	8.8
	Std. Dev.	1.6	1.6	0.2	3.7	1.8
Valles Caldera	Mean	24.3	25.1	8.3	661.6	0.2
	Std. Dev.	4.7	6.0	1.9	57.6	0.1
Soda Dam Springs	Mean	13.2	12.8	5.5	42.5	1.6
	Std. Dev.	1.4	1.7	2.5	8.1	0.6
Jemez Springs	Mean	7.6	6.5	2.9	78.8	0.7
	Std. Dev.	1.9	1.5	0.7	20.8	0.3
Indian Springs	Mean	5.2	7.7	4.2	17.8	2.5
	Std. Dev.	1.5	0.0	0.0	0.0	0.1

highlight higher Cl concentration, they also show co-variation between elements, as well as mixing of different geothermal end-members. Cl is easily modified by dissolution of salts present in Paleozoic and Mesozoic strata (Trainer et al., 2000), so plots of Li vs B, Br vs Li and Br vs B were created, discussed below.

### 4.3. Stable isotopes of D, <sup>18</sup>O and <sup>13</sup>C

Stable isotopes of D and <sup>18</sup>O from all spring locations as well as selected surface waters and aquifers in the study area are plotted in Fig. 4 (Table S3, individual springs plotted in Fig. S8 a–g). Samples that plot close to the Global Meteoric Water Line (GMWL) include the East Fork Jemez River, representative of local meteoric water runoff, as well as regional aquifer waters from the San Juan basin. Samples from the San Juan Basin are lower than any observed spring values by up to  $\delta\text{D}$  20‰ and  $\delta^{18}\text{O}$  3‰. Carbonic springs fall to the right of the GMWL and show a range of  $\delta\text{D}$ : –110.5‰ to –47.1‰ and  $\delta^{18}\text{O}$  –14.5‰ to –3.65‰. Samples from Tierra Amarilla have the greatest range ~  $\delta\text{D}$  10‰ and  $\delta^{18}\text{O}$  4‰, while samples from Jemez Springs have similar  $\delta\text{D}$ , but lower  $\delta^{18}\text{O}$  ~1–2‰.

The high and variable CO<sub>2</sub> content of these springs is used to understand their origin, mixing, and connection to geothermal fluids. The different carbon reservoirs considered as the source of CO<sub>2</sub> are: carbonates, organic (e.g. soil gas and carbon released from organic-rich sedimentary rocks), and endogenic (deep tectonic origin) carbon derived from fluids that have interacted and mixed with crust and mantle sources and circulation below the aquifer, including geothermal waters. These are represented by  $\delta^{13}\text{C}$  values of ~0, ~–28 and ~–6 respectively (Sharp, 2007). Results are shown in Table S6 and Fig. 5a.  $\delta^{13}\text{C}$  values range from  $\delta^{13}\text{C}$  = –2.47 in the Valles Caldera to –8.71 at Tierra Amarilla, and show a decrease with distance from the Valles Caldera.



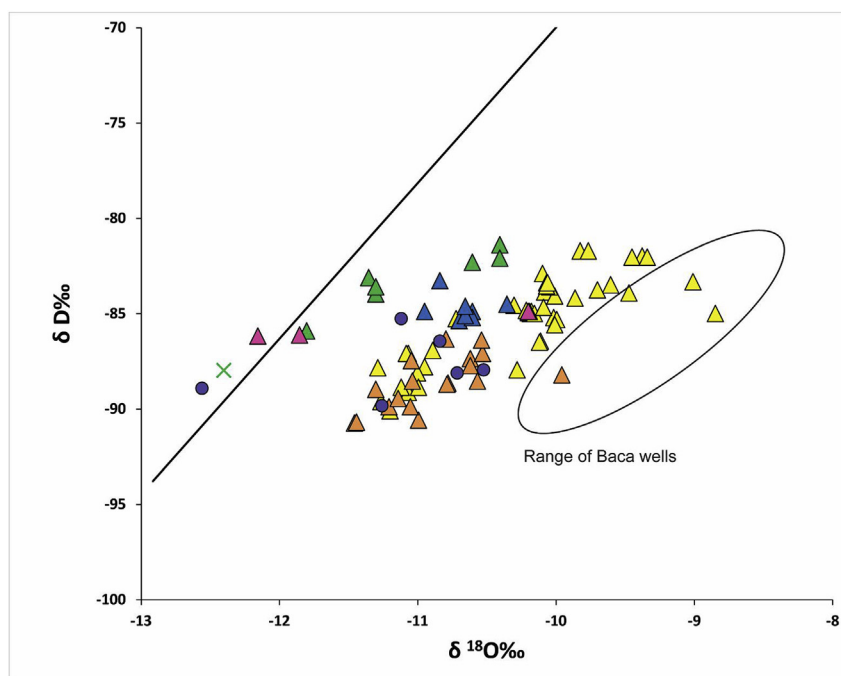
**Fig. 3.** a. Li vs Cl. Tierra Amarilla (yellow triangles), Penasco Springs (orange triangles), Kasemen Well (purple circles), Soda Dam spring (blue triangles), Jemez Springs (green triangles), Indian hot springs (pink triangle), Valles Caldera (red triangles). **3b.** B vs Cl shows a pattern similar to 3a. **3c.** Li vs B highlights the close covariance for these two trace elements between Valles Caldera springs and those more distal from the caldera. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

#### 4.4. Strontium isotopes

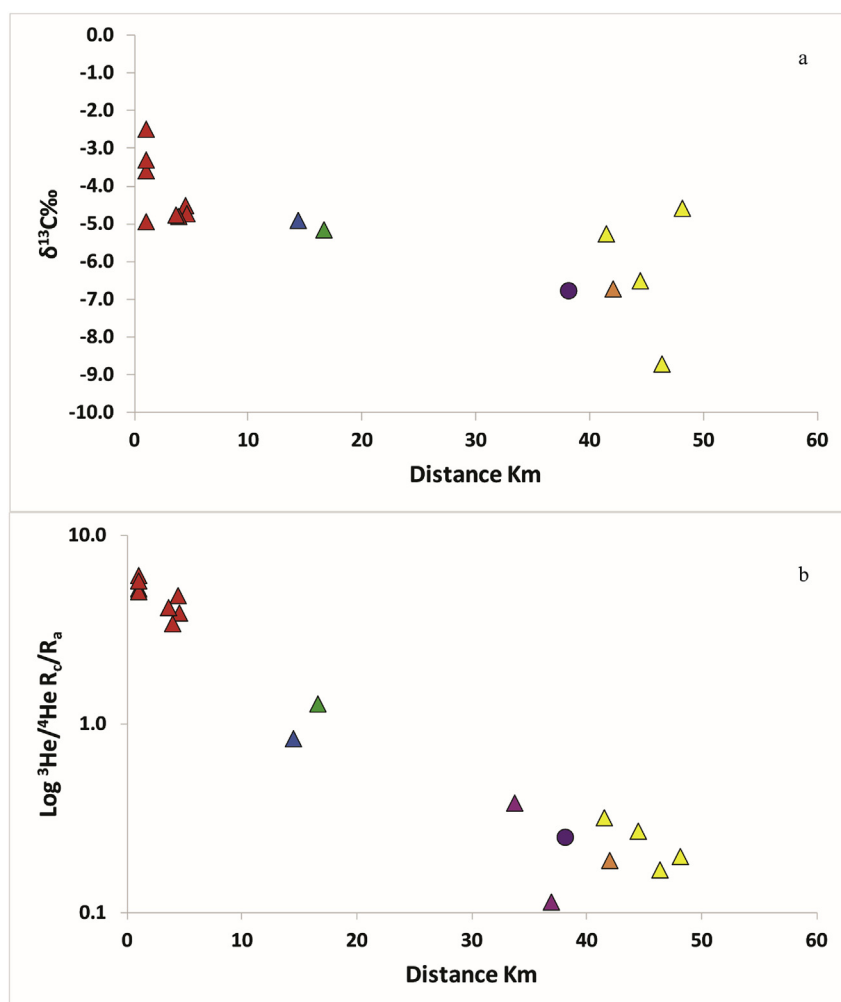
$^{87}\text{Sr}/^{86}\text{Sr}$  can indicate if groundwater has been in contact with Precambrian basement granitic rocks where  $^{87}\text{Sr}/^{86}\text{Sr}$  ranges from 0.7249 to 0.8160 (Banner, 1995; Brookins and Laughlin, 1983). In

contrast,  $^{87}\text{Sr}/^{86}\text{Sr}$  from marine carbonates have  $^{87}\text{Sr}/^{86}\text{Sr}$  closer to 0.709 (Crossey et al., 2006). Mixing between these end-members has been quantified in past studies (Crossey et al., 2006).

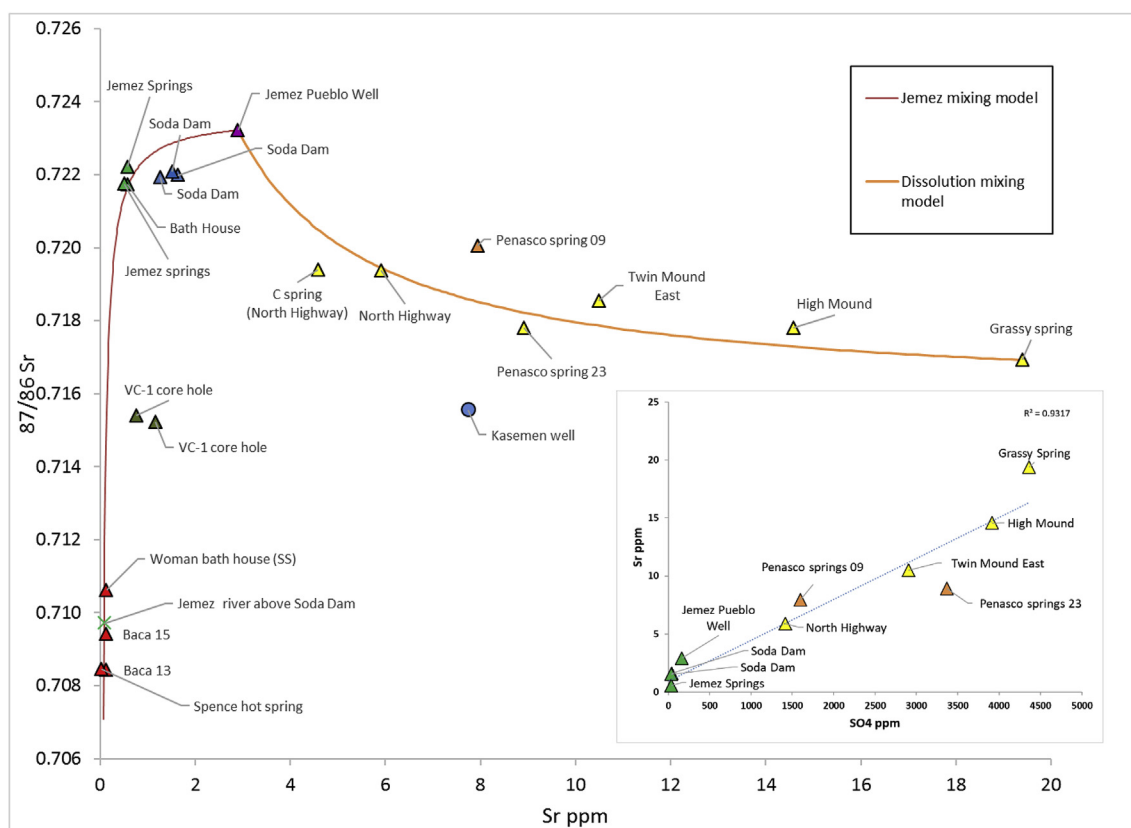
The  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration data are reported in Table S5. At Tierra Amarilla and Penasco Springs,  $^{87}\text{Sr}/^{86}\text{Sr}$  range from 0.716932 to



**Fig. 4.** Stable isotopes of deuterium and oxygen. Tierra Amarilla (yellow triangles), Penasco Springs (orange triangles), Kasemen Well (purple circles), Soda Dam spring (blue triangles), Jemez Springs (green triangles), Indian hot springs (pink triangles), East Fork Jemez River (green X) and compositional range of Valles Caldera Baca wells (black oval; see Fig. DR4g for wider range of Valles Caldera geothermal waters). Samples from the Kasemen (purple circle) well show a range of values similar to Tierra Amarilla/Penasco springs (Individual spring samples are in figure DR-3). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 5.** a.  $\delta^{13}\text{C}$  vs distance from the Valles Caldera. Tierra Amarilla (yellow triangles), Penasco Springs (orange triangles), Jemez Springs (green triangles), Soda Dam Springs (blue triangles), Valles Caldera (red triangles). Carbon isotope values decrease progressively with distance from the Valles Caldera due to mixing of endogenic and epigenic carbon sources. 5b.  $\text{Log } ^3\text{He}/^4\text{He } R_c/R_a$  vs distance from the Valles Caldera. With distance from the caldera,  $R_c/R_a$  values decrease. All values are above 0.1  $R_c/R_a$  which suggests a significant mantle helium component. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 6.** [Sr] in ppm vs  $^{87}\text{Sr}/^{86}\text{Sr}$ . Low concentration and non-radiogenic (low)  $^{87}\text{Sr}/^{86}\text{Sr}$  are seen in samples from the Valles Caldera and Jemez River (meteoric water). Soda Dam and Jemez Springs, concentration increases and  $^{87}\text{Sr}/^{86}\text{Sr}$  becomes more radiogenic (higher). Tierra Amarilla and Penasco springs have higher [Sr] and  $^{87}\text{Sr}/^{86}\text{Sr}$  values decrease with increasing distance from the Valles Caldera reflecting mixing of geothermal (Valles) waters, first mixed with Jemez Springs waters (brown curve) then with more distal groundwater at Grassy Spring (orange curve). Binary mixing models (brown and orange curves) are described in text. Note that Grassy Spring is the southwestern most of the Tierra Amarilla springs (and furthest from the Valles Caldera) and is ~50 km SW of the Valles Caldera (see Fig. S1 for detailed location of Tierra Amarilla springs). Inset -  $\text{SO}_4$  vs Sr (ppm). Samples show increasing Sr concentration with increasing  $\text{SO}_4$  concentration reflecting mixing of geothermal waters with increased volume of waters influenced by water-rock interaction with Yesso Formation salts. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

0.720044 and Sr concentration from 5.9 to 19.4 ppm. At Soda Dam and Jemez Springs  $^{87}\text{Sr}/^{86}\text{Sr}$  range from 0.709710 to 0.723217 with Sr concentration from 0.57 to 1.6 ppm. In the Valles Caldera samples range from  $^{87}\text{Sr}/^{86}\text{Sr}$  = 0.708069 to 0.708828 with Sr concentration from 0.093 to 0.26 ppm.

#### 4.5. Gas chemistry

Helium gas data from springs in the study area provide evidence of a deeply sourced connection, and help delineate water source and amount of mixing. Mantle-derived fluids from hydrothermal activity at oceanic spreading centers characterize mid-oceanic ridge basalt (MORB) asthenosphere at  $8 \pm 1 R_A$  (Graham, 2002). Stable shield areas have much lower values of ~0.02  $R_A$  (Andrews, 1985).  $^3\text{He}/^4\text{He}$  ratio > 0.1  $R_A$  in non-air-like waters (> 1.3% of MORB), are taken as evidence for the presence of mantle-derived fluids entrained by the hydrologic system (Ballentine and Burnard, 2002).  $^3\text{He}/^4\text{He}$  values measured from springs and wells in the study area are shown in Fig. 5b, (Table S6). Springs approach MORB values in the Valles Caldera, reaching 6.3  $R_A$  (79% MORB; Goff and Janik, 2002), 0.8–1.3  $R_A$  at Soda Dam and Jemez Springs, 0.1–0.4  $R_A$  at Indian springs and 0.2–0.3  $R_A$  for Tierra Amarilla and Penasco Springs.

## 5. Discussion

By identifying the chemical characteristics of end-member waters, it is possible to establish potential water sources for springs at Tierra

Amarilla/Penasco Springs. Here we assess the three hypotheses proposed-water origins from: 1) San Juan Basin aquifers, 2) young meteoric recharge from the Nacimiento Mountains, and 3) geothermal inputs.

#### 5.1. Sedimentary aquifer end-member - San Juan Basin

Samples from groundwater wells of the San Juan Basin have varying characteristics depending on which aquifers are considered, Morrison, Dakota or Gallup Aquifers. Samples from the east side of the basin show primarily Na + K/ $\text{SO}_4$  type waters, with temperatures ranging from 18 to 42 °C and pH ≈ 8.2. Stable isotopes of D and  $^{18}\text{O}$  range from  $\delta\text{D}$  –87.0‰ to –110‰ and  $\delta^{18}\text{O}$  –11.8‰ to –14.5‰. These aquifers are not present in the immediate study area, but are considered representative of groundwater moving east, from the deeper San Juan Basin toward the study area. These aquifer waters display a unique range of chemistry, which distinguishes them from both meteoric and geothermal/carbonic water (see Figs. S6g and S8g). Gas samples from the north of the basin have He isotopes (0.08–0.17 R/Ra) and are dominated by methane (Zhou et al., 2005), whereas spring gases from our study area have no detectable methane.

##### 5.1.1. Meteoric water end-member – Nacimiento Mountain recharge

The Jemez River from above Soda Dam is considered a proxy for a local meteoric water end-member for mixing purposes. Temperature range tracks atmospheric temperature, pH is ~7, salinity is very low, major ion chemistry is dominated by Ca + Na/ $\text{HCO}_3$ , and from the



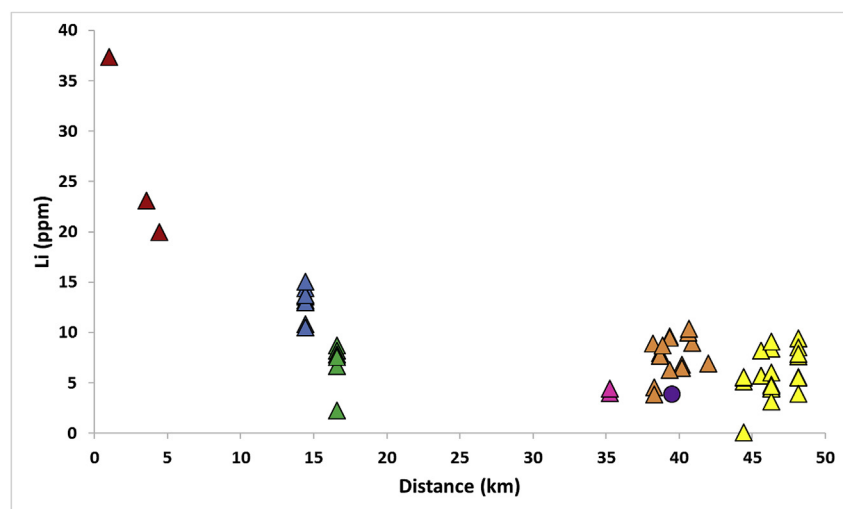


Fig. 7. Li vs distance from the Valles Caldera. Values decrease with increased distance. Tierra Amarilla (yellow triangles), Penasco Springs (orange triangles), Indian hot springs (pink triangles), Jemez Springs (green triangles), Soda Dam Springs (blue triangles), Valles Caldera (red triangles). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Piper diagram (Piper, 1944) (EFJR - Fig. 2), meteoric water is distinct from spring water samples. Stable isotopes of D and  $^{18}\text{O}$  are  $\delta\text{D} -88.0\text{‰}$  and  $\delta^{18}\text{O} -12.40\text{‰}$  and plot close to the GMWL relative to the spring samples.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is non-radiogenic  $\sim 0.709710$  and Sr concentration is low  $\sim 0.09$  ppm.

#### 5.1.2. Geothermal end-member - Valles Caldera

These waters are characterized by highest temperatures, highest  $^3\text{He}/^4\text{He}$  ratio, and  $^{13}\text{C}$  with near-mantle signatures. Sulphur Springs and the Baca Wells in the Valles Caldera ( $T \sim 214^\circ\text{C}$ ,  $R_A/R_C \sim 6$ ,  $\delta^{13}\text{C} \sim -3.8\text{‰}$ ) appears to represent the Valles Caldera end member. They anchor linear trends in water chemistry as a sodium chloride dominated water (Fig. 2), have the B, Br, Li signature of a geothermal water (Fig. 3 a–c), and the most significant  $\delta^{18}\text{O}$  enrichment of all samples (Fig. 4). In this case, the near-MORB  $^3\text{He}/^4\text{He}$  ratios from 3.39 to 6.16  $R_A/R_C$  (Goff and Janik, 2002), and the near-MORB  $\text{CO}_2/^3\text{He}$  ratio of  $1\text{--}7 \times 10^9$  (Newell et al., 2005; compared to  $2 \times 10^9$  for MORB; Graham, 2002), and the  $\delta^{13}\text{C}$  value of  $\sim -4\text{‰}$  all suggest a magmatic origin for the  $\text{CO}_2$ . A magma chamber is suggested in the western portions of the Valles Caldera (Trainer et al., 2000), and numerous recent eruptions over the last 1.6 Ma make it clear that high  $\text{CO}_2$  is an ongoing expression of the Quaternary caldera magmatism and geothermal activity.

Soda Dam, Jemez Springs and Indian Springs are discussed here as they are considered to reflect an evolved water from the Valles Caldera (Goff et al., 1981), mixing with meteoric water, and as such provide information about water which is both, chemically and geographically, closer to Tierra Amarilla and Penasco Springs. Jemez Springs show a similar chemistry to Soda Dam springs, but with greater variation and less salinity. These waters have very similar (overlapping) major and trace elements (Figs. 2 and 3), stable isotopes of  $^{18}\text{O}$  and D (Fig. 4), helium isotopes, and  $^{87}\text{Sr}/^{86}\text{Sr}$  (Fig. 6). The enrichment in  $\delta^{18}\text{O}$  and Cl, Li, B and Br, along with  $^3\text{He}$ , are typical of the geothermal end member, and together suggest a geothermal origin.

#### 5.2. Tierra Amarilla and Penasco Springs

Having defined these possible end members, the following sections describes mixing models for the spring groups.  $^3\text{He}/^4\text{He}$  provides strong evidence of a mantle connection from samples within the Valles Caldera. As distance increases from the caldera,  $^3\text{He}/^4\text{He}$  values decrease (Fig. 5b), but still suggest a mantle connection. As  $^3\text{He}$  is derived from the mantle, a connection to the Valles Caldera would provide a source of  $^3\text{He}$ , and subsequent mixing with meteoric water along the flow path and addition of  $^4\text{He}$  from the crust, would cause dilution lowering the  $^3\text{He}/^4\text{He}$  ratio. The geothermal input hypothesis is the

only option which is able to provide a source for the observed  $^3\text{He}$  and the high  $^3\text{He}/^4\text{He}$  ratio. This conclusion does not preclude some mixing with other fluid end-members examined. This discussion will now focus on explaining the water chemistry in terms of water sourced from the Valles Caldera, consider previous arguments against this hypothesis, and assess other potential end members to explain the chemistry found at Tierra Amarilla and Penasco Springs. The Kasemen well is the furthest west of the samples taken (Fig. 1 and S1), is the only well sampled at Tierra Amarilla and Penasco Springs, and is known to penetrate the Madera aquifer. As such it has a symbol unique from other Penasco Springs samples for evaluation purposes.

##### 5.2.1. Valles Caldera hydrothermal connection

The Valles Caldera hypothesis had been dismissed in the past (Goff et al., 1981), with the similarity in geochemistry being due to deep circulation of fluids and dissolution of evaporates along the Nacimiento fault in the Mesozoic to Paleozoic rocks, a geothermal system considered unique from the Valles Caldera. In particular, higher Na/Cl ratio, and lower B/Cl and Li/Na ratios in the springs at Tierra Amarilla and Penasco Springs in comparison to Soda Dam and Jemez Springs were used to draw this conclusion. However, our new data with more springs sampled, have trace element concentration ranges of Li, B and Ba comparable to Soda Dam and Jemez Spring (Fig. 3a–c). The difference in ratios previously considered, is essentially a difference in major ion concentrations of Na and Cl (Fig. S5a). These increased concentrations can be accounted for through water-rock interaction: dissolution of marine evaporites along the Nacimiento fault, a process suggested by multiple authors in the past (Goff et al., 1981; Trainer et al., 2000). Furthermore, co-variation in Li/B (Fig. 3c) also provides evidence for a mixing continuum. The majority of samples sit close to the 1:1 line, suggesting comparable processes occur. Comparing Li with distance from the Valles Caldera (Fig. 7) shows a decrease in Li with increase in distance. This is attributed to mixing with meteoric water along the flow path, diluting Li concentrations, a phenomenon witnessed in multiple tracers, discussed below. Fig. 3c suggests Tierra Amarilla and Penasco Springs plot along the mixing curve of geothermal conservative tracers that connects Valles Caldera springs/wells as one end member, with Soda Dam and Jemez Springs as intermediate points, with meteoric and potentially sedimentary aquifer units as the other end members. Fig. 3a and b shows that fluid mixing and water-rock interaction in the areas distal to the caldera are needed to explain non-linear relationships.

The isotopic enrichment of  $^{18}\text{O}$  of water at Tierra Amarilla and Penasco Springs was suggested to follow a different trend to the geothermal waters sourced from the Valles Caldera (Goff et al., 1981). While the sample range appears to have an offset slope, as with the

trace elements, the new data have an overlapping range, clearly different from the distinct spring clusters reported previously (Goff et al., 1981; Trainer et al., 2000). Similarities in stable isotope data of deuterium and oxygen (Fig. 4) suggest a connection to Soda Dam and Jemez Springs if not the Valles Caldera, and potentially, the smaller geothermal reservoirs along the Jemez Fault, proposed by Goff et al. (1981), could be a source of mixing water for the study area, and be considered as being represented by water at Soda Dam springs or Jemez Springs. This is a somewhat semantic argument as Soda Dam and Jemez Springs are considered to be sourced from the Valles Caldera.

Samples from all spring groups fall away and to the right of the GMWL, indicating higher  $^{18}\text{O}/^{16}\text{O}$  values typically associated with high-temperature water-rock isotopic exchange. Spring groups' samples are considered to be formed through mixing between a geothermally evolved end member represented, by the Baca wells and meteoric waters, similar to the East Fork Jemez River. The overall array (all triangles) has a lower slope than evaporation and hence is interpreted to reflect variable water-rock interaction characteristic of geothermal fluids.

The hydrothermal outflow plume from the Valles Caldera provides an end member source for mixing of water at Tierra Amarilla and Penasco Springs, utilizing the fault network which connects the two areas. This is highlighted through the application of strontium isotopes, and will be evidenced by radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values and increased strontium concentration ([Sr]). Strontium isotope ratios show an initial increase and then decrease with distance from the Valles Caldera, while strontium concentrations display a continuous increase. Samples form distinct groups based on spatial variation (Fig. 6). The Jemez River sample from above Soda Dam (local meteoric water) and the Valles Caldera have low [Sr], < 1 ppm, and non-radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values < 0.710. Meteoric water is low in all dissolved solids and the  $^{87}\text{Sr}/^{86}\text{Sr}$  values for the Valles Caldera are due to the host rocks: Banded Tuff, andesite and rhyolite (Vuataz et al., 1988). Samples from Soda Dam and Jemez Springs have [Sr] up to 4 ppm and more radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values ~ 0.723. The increased [Sr] is due to water rock interaction along the flow path with the higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values indicating the water has been in contact with Precambrian basement granites ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.7249–0.8163; Brookins and Laughlin, 1983) through deep circulation or has mixed with fluids that have risen from depth. Samples from Tierra Amarilla and Penasco Springs have the highest [Sr], from 5 to 20 ppm, but  $^{87}\text{Sr}/^{86}\text{Sr}$  values lower than at Soda Dam, between 0.715 and 0.720. The increases in [Sr] with distance from the Valles Caldera are explained by dissolution of relatively soluble sedimentary components (calcite, dolomite and gypsum) along the flow path. However, decrease in  $^{87}\text{Sr}/^{86}\text{Sr}$  values indicate the addition of Sr with lower  $^{87}\text{Sr}/^{86}\text{Sr}$  is occurring; we interpret this as reflecting dissolution of marine carbonates and evaporates ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.7088 for Madera limestone, Vuataz et al., 1988).

Simple binary mixing models for different end members can be used to model the mixing process (Fig. 6). Using equations from Faure (1986), the  $^{87}\text{Sr}/^{86}\text{Sr}$  value of a fluid with 2 components (A and B) can be calculated using:

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{M}} = A/\text{Sr}_{\text{M}} + B$$

Where  $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{M}}$  is the Sr isotopic ratio in the mixture,  $\text{Sr}_{\text{M}}$  is the [Sr] in the mixture (found using,  $\text{Sr}_{\text{M}} = \text{Sr}_{\text{A}} f_{\text{A}} + \text{Sr}_{\text{B}} (1 - f_{\text{A}})$  where  $\text{Sr}_{\text{A}}$  and  $\text{Sr}_{\text{B}}$  are [Sr] in the mixing components A and B respectively, and  $f_{\text{A}}$  is the mixing fraction of A, from 0 to 1), and

$$a = \text{Sr}_{\text{A}} * \text{Sr}_{\text{B}} [(^{87}\text{Sr} / ^{86}\text{Sr})_{\text{B}} - (^{87}\text{Sr} / ^{86}\text{Sr})_{\text{A}}] / \text{Sr}_{\text{A}} - \text{Sr}_{\text{B}}$$

$$b = \text{Sr}_{\text{A}}(^{87}\text{Sr} / ^{86}\text{Sr})_{\text{A}} - \text{Sr}_{\text{B}}(^{87}\text{Sr} / ^{86}\text{Sr})_{\text{B}} / \text{Sr}_{\text{A}} - \text{Sr}_{\text{B}}.$$

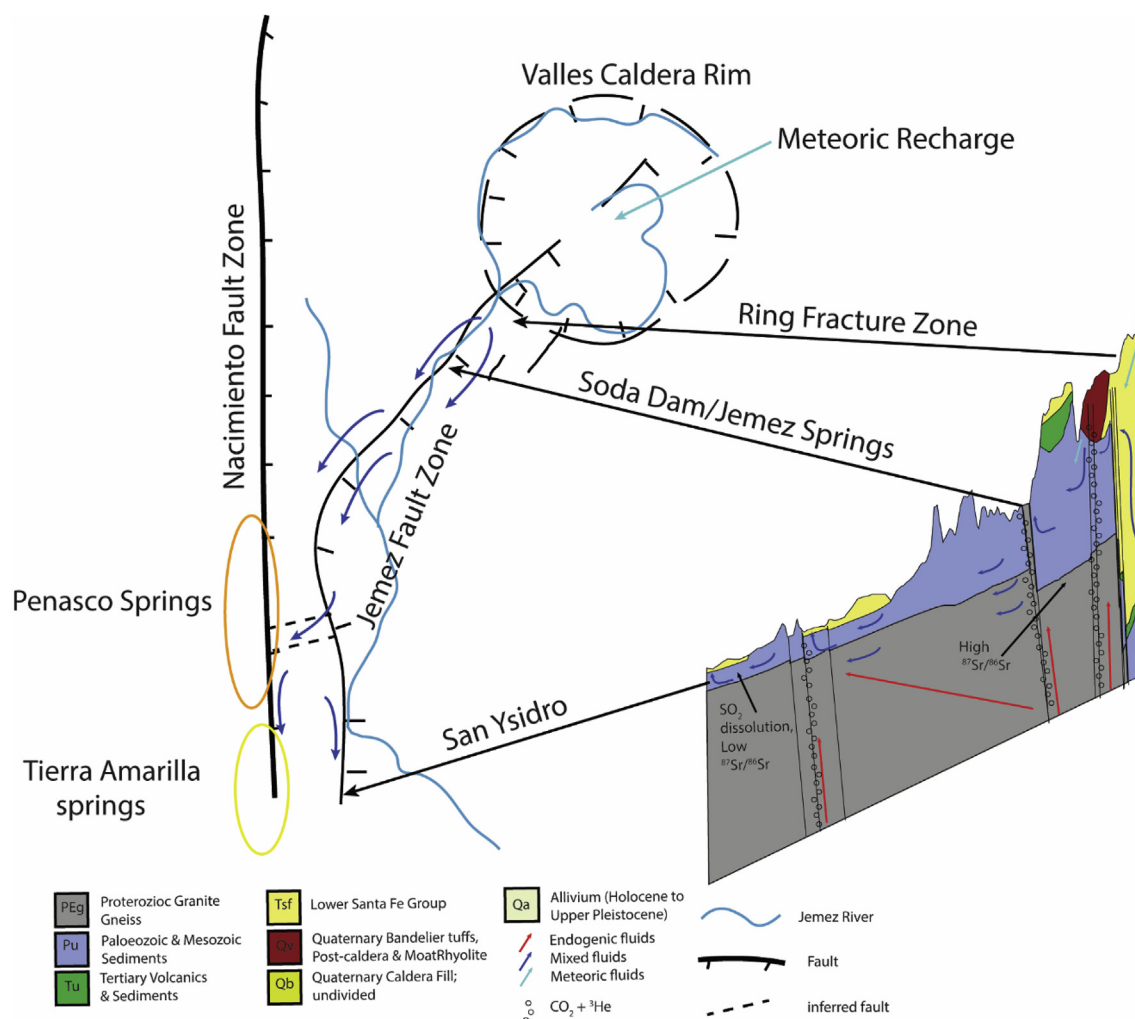
Two different models are presented. 1) The Jemez mixing model (solid brown line) uses an initial non-radiogenic end member from the Valles Caldera ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.70784), and Jemez Pueblo well (Indian hot springs) end member ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.723216) 2) The dissolution model

(solid orange line) uses the Jemez Pueblo well as its initial end member and Grassy Springs ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.716926) as the other. Samples from the Valles Caldera, Soda Dam springs and Jemez Springs fall along the Jemez mixing model. This model explains the [Sr] and  $^{87}\text{Sr}/^{86}\text{Sr}$  evolution of water from the Valles Caldera to the Jemez Pueblo well. Initially, water has low [Sr] and non-radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$ , it comes into contact with basement granites in the fault zone, where dissolution of Sr occurs, increasing [Sr] with radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values. If springs in the Tierra Amarilla/Penasco Springs region are sourced in part from the Valles Caldera, then similar, or higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values would be expected, however this is not the case. As discussed above, dissolution of Paleozoic rocks along the flowpath is suggested as an explanation for the high Cl values found in these springs. This process can also explain the higher [Sr], and associated lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values. The dissolution of marine carbonates and evaporates can increase [Sr], while lowering  $^{87}\text{Sr}/^{86}\text{Sr}$  values due to the non-radiogenic nature of the Sr,  $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.709$ . This is highlighted in Fig. 6 inset, [Sr] vs  $[\text{SO}_4]$ , where co-variation occurs. Further evidence of gypsum dissolution is found in the major ion chemistry. Water from Soda Dam springs and Jemez Springs plot along a mixing line with end-members from the Valles Caldera and East Fork Jemez River with the springs being the product of mixing between geothermal and meteoric water (Fig. 2). If this approach is attempted for samples from Tierra Amarilla and Penasco Springs, the potential end members are less clear. Focusing on the anion triangle, the Valles Caldera/Jemez River mixing line is apparent, but a secondary mixing line, increasing relative sulfate, is needed to move from Soda Dam/Jemez Springs, passing through Indian hot springs, to Tierra Amarilla/Penasco Springs. A possible way to achieve this is through the dissolution of gypsum, a rock present locally at Tierra Amarilla/Penasco Springs, but less so at Soda Dam and Jemez Springs.

Fig. 5a shows how  $\delta^{13}\text{C}$  varies with distance from the Valles Caldera. Values decrease with increasing distance. Values fall within the range of a mantle signature (–4 to –8‰), and the steady decrease away from the Valles Caldera can be attributed to addition of an organic carbon end member (–28‰), which is added along the flow path due to mixing with meteoric water which will have percolated through soil layers. This is reflected in modeled percent organic carbon contribution, which shows an increase in the organically-derived component of dissolved inorganic carbon with distance from the Valles Caldera, up to 24% at Tierra Amarilla (McGibbon, 2015).

### 5.2.2. San Juan Basin connection

Water from the eastern San Juan Basin is hypothesized to be moving east (Frenzel and Lyford, 1982, Fig. 1); and, as such is postulated as a source of water for the springs at Tierra Amarilla and Penasco Springs. Lack of water and gas data from the eastern side of the basin, particularly from deeper aquifers, such as the Madera, makes this difficult to establish. The differences in Cl concentrations that are used to suggest different water sources could be altered through the addition of a high Cl end-member water, the source of which would be the sedimentary aquifer waters of the San Juan Basin, with the high Cl being attributed to water-rock interaction, particularly the dissolution of evaporites. Samples from the eastern San Juan Basin are considered aquifer waters, and are interpreted to be dominated by meteoric water, which have evolved chemically, from a major ion point of view, with stable isotopes suggesting no mixing with endogenic water. The aquifer waters are expected to have low  $^3\text{He}/^4\text{He}$ ,  $\delta^{13}\text{C}-\text{CO}_2$  close to zero, from carbonates, with gases dominated by methane (Zhou et al., 2005). There is no manifestation of this in the waters at Tierra Amarilla or Penasco Springs. Gas samples show no evidence of detectable methane, which is associated in dissolved gases from the San Juan basin. As such, we interpret San Juan basin aquifer waters to have a negligible contribution to springs venting along the Nacimiento fault.



**Fig. 8.** Schematic model of fluid movement and evolution, plan view and cross-section (modified from Goff 2009) from the Valles Caldera to Tierra Amarilla springs. Meteoric water (light blue arrow) in the Valles Caldera recharges the geothermal system where water circulates at depth before rising (red arrows), and discharging from the southeast of the caldera, along the Jemez fault zone. As water flows along the fault zone, it evolves due to water rock interaction (dark blue arrows), mixing with other waters before discharging at multiple locations, Soda Dam and Jemez Springs. These waters are distinct due to low [Sr], [SO<sub>4</sub>], and high <sup>87</sup>Sr/<sup>86</sup>Sr. At Tierra Amarilla and Penasco springs, dissolution of SO<sub>4</sub> increases [SO<sub>4</sub>], with associated increases in [Sr] and decrease in <sup>87</sup>Sr/<sup>86</sup>Sr, explaining the distinct chemistry found at these springs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

### 5.2.3. Nacimiento Mountains meteoric water connection

The springs at Tierra Amarilla and Penasco Springs clearly mix with meteoric water, but the <sup>3</sup>He/<sup>4</sup>He, <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>13</sup>C–CO<sub>2</sub> values all indicate there has to be the addition of a deeper water component. In the Tierra Amarilla spring group, variation in water chemistry occurs only at North Highway, a shift in anions, decrease in SO<sub>4</sub>, increase in HCO<sub>3</sub>, and greater temperature and geochemical variation than the southern springs along the Nacimiento fault. The greater range in North Highway is attributed to the location being slightly aside the fault at the toe of the slope and could be due to local slope recharge which is not seen south of the river. The location away from the fault could potentially contribute less of a deep component, but with mixing of meteoric water from the Agua Zarca dip-slope, suggested by the increased HCO<sub>3</sub>. Thus, for this spring we incorporate elements of the hypothesis of Hart (2001) for groundwater recharge from the Agua Zarca.

## 6. Conclusion

We investigated three hypotheses to identify the source of water for a series of springs discharging along the Nacimiento fault. Based on the trace elements, isotopes of D, <sup>18</sup>O, <sup>3</sup>He/<sup>4</sup>He, <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>13</sup>C–CO<sub>2</sub>, and groundwater contour flow lines, Tierra Amarilla and Penasco

Springs are interpreted here to be a combination of geothermal water sourced from the Jemez Geothermal system, meteoric recharge-pre-dominantly from along the flow path, with a small component of dip-slope recharge for North Highway spring with negligible contribution from the San Juan Basin based on the absence of methane (Fig. 8). The meteoric component may differ subtly between spring groups, but it is the percentage geothermal (endogenic) end member plus the nature of water-rock interaction that dictates the observed water chemistry variability. Tierra Amarilla and Penasco Spring waters are distal parts of the Valles Caldera geothermal system in terms of CO<sub>2</sub>, helium, and geothermal tracers. Gas analysis shows that the endogenic volatiles include a component from the Earth's mantle and that excess CO<sub>2</sub> is likely the carrier gas for deeply sourced crust and mantle volatiles that are geochemically potent and that degrade water quality in these springs. Helium isotopes also suggests a deeply sourced component to the springs with the observation of elevated <sup>3</sup>He/<sup>4</sup>He, which decreases with distance from the Valles Caldera. Strontium isotopes indicate that spring water has been in contact with basement granites; however dissolution of SO<sub>4</sub> increases Sr concentration and decreases <sup>87</sup>Sr/<sup>86</sup>Sr values at Tierra Amarilla and Penasco Springs which is explained by water-rock interaction with Yeso and Todilto formations. Geochemistry of spring water, and map geometries suggests a fault connection



between springs sampled at Soda Dam and Jemez Springs and spring groups at both Tierra Amarilla and Penasco Springs. Based on trace element ratios, and isotopes of carbon, helium and strontium, the latter of which suggest that geothermal fluids move along NW-trending fault pathways across the Nacimiento Mountain block, faults demonstrably connect spring groups and allow mixing in complex proportions. The confined or semi-confined fault conduits provide connectivity within and between springs and spring systems and help explain geochemical similarities between Tierra Amarilla and Penasco Springs.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.apgeochem.2018.08.015>.

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